

E/C

## TENT COOPERATION TRE Y

PCT

## NOTIFICATION RELATING TO PRIORITY CLAIM

(PCT Rules 26bis.1 and 26bis.2 and  
Administrative Instructions, Sections 402 and 409)

From the INTERNATIONAL BUREAU

To:

WISHART, Ian, Carmichael  
Johnson Matthey Technology Centre  
Blounts Court  
Sonning Common  
Reading RG4 9NH  
ROYAUME-UNI

Date of mailing (day/month/year) 27 October 1999 (27.10.99)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference PFC 1428 PCT	
International application No. PCT/GB99/02935	International filing date (day/month/year) 03 September 1999 (03.09.99)
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al	

The applicant is hereby **notified** of the following in respect of the priority claim(s) made in the international application.

1. ☒ **Correction of priority claim.** In accordance with the applicant's notice received on: 25 October 1999 (25.10.99), the following priority claim has been corrected to read as follows:  
GB 16 October 1998 (16.10.98) 9822569.1  
☐ even though the indication of the number of the earlier application is missing.  
☐ even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:
2. ☐ **Addition of priority claim.** In accordance with the applicant's notice received on: , the following priority claim has been added:  
☐ even though the indication of the number of the earlier application is missing.  
☐ even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:
3. ☐ As a **result of the correction and/or addition** of (a) priority claim(s) under items 1 and/or 2, the (earliest) priority date is:
4. ☐ **Priority claim considered not to have been made.**  
☐ The applicant failed to respond to the Invitation under Rule 26bis.2(a) (Form PCT/IB/316) within the prescribed time limit.  
☐ The applicant's notice was received after the expiration of the prescribed time limit under Rule 26bis.1(a).  
☐ The applicant's notice failed to correct the priority claim so as to comply with the requirements of Rule 4.10.  
The applicant may, before the technical preparations for international publication have been completed and subject to the payment of a fee, request the International Bureau to publish, together with the international application, information concerning the priority claim. See Rule 26bis.2(c) and the PCT Applicant's Guide, Volume I, Annex B2(IIb).
5. ☐ In case where **multiple priorities** have been claimed, the above item(s) relate to the following priority claim(s):
6. A copy of this notification has been sent to the receiving Office and  
☒ to the International Searching Authority (where the international search report has not yet been issued).  
☒ the designated Offices (which have already been notified of the receipt of the record copy).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Dominique DELMAS
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
 United States Patent and Trademark  
 Office  
 Box PCT  
 Washington, D.C.20231  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing</b> (day/month/year) 07 June 2000 (07.06.00)	
<b>International application No.</b> PCT/GB99/02935	<b>Applicant's or agent's file reference</b> PFC 1428 PCT
<b>International filing date</b> (day/month/year) 03 September 1999 (03.09.99)	<b>Priority date</b> (day/month/year) 16 October 1998 (16.10.98)
<b>Applicant</b> FONGALLAND, Dharshini, Chryshantha et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

10 May 2000 (10.05.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer S. Mafla Telephone No.: (41-22) 338.83.38
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## P. NT COOPERATION TREATY

From the INTERNATIONAL BUREAU

**PCT****NOTIFICATION OF WITHDRAWAL OF  
INTERNATIONAL APPLICATION OR  
DESIGNATIONS**(PCT Rule 90bis.1 and 90bis.2 and  
Administrative Instructions, Section 415(a))

To:

W.P. THOMPSON & CO.  
Coopers Building  
Church Street  
Liverpool L1 3AB  
ROYAUME-UNI

Date of mailing (day/month/year) 08 October 1999 (08.10.99)		
Applicant's or agent's file reference NMM/P66706WO		<b>IMPORTANT NOTIFICATION</b>
International application No. PCT/GB99/02835	International filing date (day/month/year) 27 August 1999 (27.08.99)	Priority date (day/month/year) 27 August 1998 (27.08.98)
Applicant FORTH TOOL & VALVE LIMITED		

1. The applicant is hereby notified that, except as to any designated State in which national processing or examination has already started upon the express request of the applicant:

- ☐ the international application
- ☒ the designations of the following States:
- ☐ for an ARIPO patent (specify "all States" or, if the withdrawal concerns only some States, specify those States only by indicating the two-letter country codes): all states
  - ☐ for a Eurasian patent
  - ☐ for a European patent (specify "all States" or, if the withdrawal concerns only some States, specify those States only by indicating the two-letter country codes):
  - ☒ for an OAPI patent
  - ☐ for a national patent (specify the States by indicating the two-letter country codes):  
AF, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES,  
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU,  
LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,  
TT, UA, UG, US, UZ, VN, YU, ZA, ZW

has (have) been withdrawn on the date of receipt of the notice effecting withdrawal as indicated below:

24 September 1999 (24.09.99)

2. The notice effecting withdrawal reached the International Bureau

- ☒ before the completion of the technical preparations for publication and, consequently, there will be no international publication:
- ☐ of the international application.
  - ☒ of the designations specified above.
- ☐ after the completion of the technical preparations for publication and, consequently, the withdrawal could not be taken into account for the international publication.

3. The receiving Office and, if they are affected by the withdrawal, the designated (or elected) Offices, the International Searching Authority and the International Preliminary Examining Authority, have been informed accordingly.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Ingrid Aulich
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

WISHART, I.  
WISHART, Ian, Carmichael  
Johnson Matthey Technology Centre  
Blounts Court  
Sonning Common  
Reading RG4 9NH  
GRANDE BRETAGNE

**RECEIVED**

31 JAN 2001

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year) 29.01.2001

Applicant's or agent's file reference  
PFC 1428 PCT

## IMPORTANT NOTIFICATION

International application No.  
PCT/GB99/02935

International filing date (day/month/year)  
03/09/1999

Priority date (day/month/year)  
16/10/1998

Applicant  
JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

### 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Hardy Magliano, N

Tel. +49 89 2399-8151



# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>PFC 1428 PCT</b>		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. <b>PCT/GB99/02935</b>	International filing date (day/month/year) <b>03/09/1999</b>	Priority date (day/month/year) <b>16/10/1998</b>
International Patent Classification (IPC) or national classification and IPC <b>C08J5/22</b>		
Applicant <b>JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.</b>		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input checked="" type="checkbox"/> Certain documents cited</li> <li>VII <input checked="" type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>		
Date of submission of the demand  <b>10/05/2000</b>		Date of completion of this report  <b>29.01.2001</b>
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer  <b>Contet, F</b>  Telephone No. +49 89 2399 8671



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/02935

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

**Description, pages:**

1-15 as originally filed

**Claims, No.:**

1-18 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
  - ☐ the language of publication of the international application (under Rule 48.3(b)).
  - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
  - ☐ filed together with the international application in computer readable form.
  - ☐ furnished subsequently to this Authority in written form.
  - ☐ furnished subsequently to this Authority in computer readable form.
  - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:
- ☐ the description, pages:
  - ☐ the claims, Nos.:
  - ☐ the drawings, sheets:
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02935

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	3-5,14-16
	No:	Claims	1,2,6-13,17,18
Inventive step (IS)	Yes:	Claims	
	No:	Claims	3-5,14-16
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

## VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

**see separate sheet**

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**I- Novelty :**

**1.1 : Claims 1 to 9 :**

The Examining authority still considers D1 = US-A-5 523 181 as closest prior art. The comments made in Item VIII should be taken into consideration. Thus, D1, Claims 1, 3 and 5, discloses the preparation of a polymer solid-electrolyte composition useful in a fuel cell (col.3, l.43-53). The layer thus obtained contains fine particles of silica (size  $\leq 0.1\mu\text{m}$ ) and/or fibrous silica fibres (diameter  $\leq 0.6\mu\text{m}$ ). The fibres are "in an amorphous crystalline structure" and have a size in the range disclosed (compare D1, col.3, line 66 to col.4, l.46 and col.6, l.60-64 and the present application, p.4, l. 16-24). The polymer can be perfluorosulfonic acid (col.4, l.47 - 54).

The relationships between the fibres size, their area and amount and the ionic conductivity was also disclosed in the same passages.

Present Claim 1 defines " a substrate, suitable for the preparation of a composite membrane ...", but not the composite itself. The feature "suitable .....membrane", is not clear (see point VIII) and cannot establish a difference between present Claim 1 and the prior art D1. The meaning of the term "substrate" is also very broad.

Thus the substrate according to Claims 1,2 and 6-9, comprising a porous matrix of fibres bound with a binder, which according to present Claim 6, can be a polymeric material is not distinguished from the layer of a polymer solid-electrolyte composition disclosed in D1.

**1.2 : Claims 10 to 13 and 17,18 :**

D1, Fig.1 and 2 and Col.14-54 is novelty destroying for the subject-matter of present Claims 10, 17 and 18.

Further characterisation of a chemical product by means of a parameter may be allowable provided that this parameter can be clearly and reliably determined either by indications in the description or by objective procedures which are usual in the art. Further the claim should include the method of measurement or at least a reference to the description. Further the fact that this feature has not been



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/GB99/02935

measured in the prior art D1 might disguise lack of novelty .

Having regard to the membrane thickness, attention is drawn to the value 150µm disclosed in D1, Ex.4.

The subject-matter of present Claims 10-13 and , 17 and 18 is not new over D1.

**1.3 :** The process of Claims 14 to 16 differs from D1 in the use of an aqueous slurry containing the fibres instead of an isopropanol slurry and is thus formally new over D1.

**II- Inventive step:**

The composition of Claims 3 and 4 differs from D1 only in that a mixture of silica fibres has been used instead of silica particles and fibres in an amorphous crystalline structure.

The problem underlying the present application can be regarded as to provide further composite ion-exchange membranes for fuel cell having improved dimensional stability and handling without compromising the ionic conductivity (page 3, paragraph 2).

As explained above the relation ship between ionic conductivity and the use of SiO<sub>2</sub> fibres was already disclosed in D1.

Having regard to D1, Claim 1, line 29 and col.4, l.28-33, the argument brought forward that "D1 does not teach that incorporation of silica at any amount improves ionic conductivity" is not understood since neither an amount feature is claimed nor the alleged effect is shown in the Examples.

Therefore, the alleged effect is considered as expected in view of D1.

A further alleged effect, that dimensional stability can be improved by the incorporation of a silica matrix has only been demonstrated over polymer membranes that do not contain any silica fibres and not over D1.

The process cannot be deemed to be inventive since a relationship between differing feature and an unexpected property of the resulting product has not been demonstrated.

**Industrial applicability :**

Preparation of a composite ion-exchange membrane for fuel cell.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02935

**Re Item VI**

**Certain documents cited**

Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
EP-A-0875 524	04.11.1998	16.04.1998	25.04.1997

No unified criteria exist in the PCT, but the EPO for instance will consider this teaching as relevant (especially Claims 1,2,5,7,14-16, 21, 23 and 26), provided it will be supplied to the European Patent Office in one of its official languages and the national fee provided for in Article 22, paragraph 1 or Article 39, paragraph 1 of the Cooperation Treaty has been paid.

**Re Item VII**

**Certain defects in the international application**

The Applicant has not explained why he does not consider the document D1 as closest prior art. Thus the requirements of Rule 5.1(a)(ii) PCT, that the relevant background art disclosed in this very relevant document D1 should be mentioned in the description, are not fulfilled.

**Re Item VIII**

**Certain observations on the international application**

**Claims 1 and 2 :**

In present Claim 1, the feature "suitable .....membrane", does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The claim attempts to define the subject-matter in terms of the result to be achieved which merely amounts to a statement of the underlying problem. The technical features necessary for achieving this result should be added.

The relative term "mixed" in the expression "mixed amorphous silica fibres" used in the Claims has no well-recognised meaning and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of this claim unclear (Article 6 PCT).

The same objection applies to the term " micro-fine" disclosed in Claim 2.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C08J 5/22, H01M 8/10</b>		<b>A1</b>	(11) International Publication Number: <b>WO 00/23510</b>
			(43) International Publication Date: 27 April 2000 (27.04.00)
(21) International Application Number: PCT/GB99/02935		(81) Designated States: CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 3 September 1999 (03.09.99)			
(30) Priority Data: 9822569.1 16 October 1998 (16.10.98) GB		<b>Published</b> <i>With international search report.</i>	
(71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): FONGALLAND, Dharshini, Chryshantha [LK/GB]; 174 Windsor Road, Slough SL1 2JD (GB). GASCOYNE, John, Malcolm [GB/GB]; Lyduska, Routs Green, Bledlow Ridge, High Wycombe, Bucks HP14 4BB (GB). RALPH, Thomas, Robertson [GB/GB]; 94 Shaftesbury Road, Reading, Berkshire RG30 2QJ (GB).			
(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).			
(54) Title: SUBSTRATE			
(57) Abstract			
<p>A substrate, suitable for the preparation of a composite membrane, which substrate comprises a porous matrix of fibres, characterised in that the fibres comprise mixed amorphous silica fibres that are bound with a binder; a composite membrane comprising the substrate and a process for the preparation of the substrate and composite membrane is disclosed.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
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EE	Estonia						

## SUBSTRATE

The present invention relates to a substrate for a composite membrane that is of use in electrochemical devices, particularly fuel cells, and a process for the manufacture of the substrate and composite membrane.

Electrochemical cells invariably comprise an ion-conducting electrolyte and two electrodes, the anode and cathode, at which the desired electrochemical reactions take place. Electrochemical cells may be found in a range of devices, for example fuel cells, batteries, sensors, electrodialysis reactors and electrolytic reactors. They have a diverse range of applications, including the electrolysis of water, chemical synthesis, salt splitting, water purification, effluent treatment and metal finishing, among others.

A fuel cell is an energy conversion device that efficiently converts the stored chemical energy of its fuel into electrical energy. It does so by combining either hydrogen, stored as a gas or methanol, stored as a liquid or a gas, with oxygen to generate electrical power. The hydrogen or methanol is oxidised at the anode and oxygen is reduced at the cathode. Both electrodes are of the gas diffusion type. The electrolyte has to be in contact with both electrodes, and may be acidic or alkaline, and liquid or solid, in nature. In proton exchange membrane fuel cells (PEMFC), the electrolyte is a solid, ion-conducting, *i.e.* a proton-conducting, polymer membrane. The membrane is commonly based on a copolymer of perfluorosulphonic acid and tetrafluoroethylene. The combined structure formed from the membrane and the two gas diffusion electrodes is known as the membrane electrode assembly (MEA).

25

Conventionally, solid ion-conducting membrane electrolytes useful in fuel cells and other devices are selected from commercially-available membranes, for example perfluorinated membranes sold under the trade names Nafion® (E I DuPont de Nemours and Co.), Aciplex® (Asahi Chemical Industry) and Flemion® (Asahi Glass KK). For application in the PEMFC, they are typically below 200µm in thickness to ensure a high level of ionic conductivity. One of the problems experienced with these conventional proton-conducting membranes used for PEM fuel cell construction, is the dimensional changes that occur as the

30

level of water content (hydration) of the membrane changes. This is a particular problem during fabrication of the MEA, in which the membrane is typically in a highly hydrated form, as the stresses produced by changes in hydration during the conventionally-employed thermal bonding process can be large enough to break the bond between either the catalyst and the  
5 membrane or the catalyst and the substrate. Furthermore, these dimensional changes lead to considerable difficulties in handling membranes during the fabrication of MEAs, particularly large area MEAs in excess of, for example, 500cm<sup>2</sup>. The thinner the membrane, the more difficult the handling becomes.

10 Yet further, it is current practice that most MEAs are fabricated as single items, with areas of, for example, 500cm<sup>2</sup> in a batch-type process. It is critical to the successful commercialisation of the PEMFC that lower cost, high volume, MEA manufacturing processes be developed in the future, such as a continuous fabrication process. The problem of dimensional change of the membrane with changes in hydration on a continuous process,  
15 which may employ membranes of many hundreds of metres in length, would then be an even more serious issue, and would add significant complications and cost to the manufacturing process.

With thicker types of membrane (*e.g.* >350µm) developed for other applications, it has  
20 been possible to incorporate 'macro' reinforcing materials, such as woven polytetrafluoroethylene (PTFE), to minimise such dimensional changes. However, these thicker materials have too low an ionic conductivity to be of use in the PEMFC. US patent 5,547,551 describes the fabrication of ultra-thin reinforced membranes, below 25µm in thickness, comprising proton-exchange polymeric material incorporated into an expanded porous PTFE  
25 membrane. According to Kolde *et al*, Electrochemical Society Proceedings 95 (23) 193-201 (1995), these reinforced membranes have considerably improved dimensional stability compared to the conventional non-reinforced membranes, such as Nafion® 117 which shows shrinkage upon dehydration from the hydrated state. However, such materials have a higher specific resistance (*i.e.* lower ionic conductivity) by a factor of at least two than a non-  
30 reinforced pure proton-conducting membrane such as Nafion® 117.

The higher specific resistance of the above reinforced membranes means that, in practice, they must be much thinner than the equivalent pure proton-conducting membrane to maintain the same overall conductivity and thus cell performance. However, reducing the thickness of the membrane reduces the advantages that a reinforced membrane can provide.

5 For example, there is a limit to the extent to which the thickness of the membrane can be reduced, since the durability and longevity can also decrease, and reactant gas cross-over through the membrane is more liable to occur, leading to a reduction in cell performance. Furthermore, the problems associated with dimensional stability and handling for MEA fabrication can be exacerbated with thinner membranes.

10

There is therefore the need to overcome the disadvantages of conventional pure and prior art reinforced membranes, by providing a novel composite ion-exchange membrane having a significantly improved dimensional stability and satisfactory handling without compromising the ionic conductivity and reactant gas cross-over parameters. Furthermore, 15 there is a need to take account of the likely process(es) by which the membrane would be manufactured in the future in choosing an appropriate membrane composition. In particular, with the prospect of continuous fabrication processes mentioned above, it is not only the structure of the membrane that may be critical. In a composite membrane generally comprising a porous substrate of fibres impregnated, coated or otherwise associated with the ion-conducting polymer (*e.g.* Nafion®), the strength and stability of the substrate itself would 20 be an important factor.

Accordingly, the present invention provides a substrate, suitable for the preparation of a composite membrane, which substrate comprises a porous matrix of fibres, characterised 25 in that the fibres comprise mixed amorphous silica fibres that are bound with a binder.

The amorphous silica for use in the substrate according to the invention is to be distinguished from crystalline quartz, although there is a tendency in an industrial context for the terms "quartz" and "silica" to be used interchangeably. Although both are chemically 30 silicon dioxide, quartz is the crystalline form and is both hard and brittle, whereas the fibrous materials (the amorphous silica for use in the substrate of the invention) are made from either

natural or synthetic quartz, and are amorphous and glass like in character, having no crystalline structure.

By "mixed amorphous silica fibres" is meant a mixture of both one or more micro-fine  
5 amorphous silica fibres and one or more of chopped strands of amorphous silica. For example, chopped silica fibres are available from Quartz et Silice BP, France under the trade name Quartzel. The base filament is available as a continuous fibre in 14 $\mu$ m, 9 $\mu$ m or 7 $\mu$ m diameters and can be supplied as chopped strands in a range of lengths such as 20mm chopped silica fibres. Silica microfibres are available from Johns Manville Insulation Group, Denver, USA,  
10 under the trade name of Q-Fibre, such as Q-Fibre Type 106. These are available in a range of nominal fibre diameters from 0.4 $\mu$ m to 4 $\mu$ m. The amount of microfibre and chopped fibres in the mixture is in the range of from 95 to 5% and 5 to 95% by weight of the mixture, respectively. Preferably, the amounts are 90 to 10% and 10 to 90% w/w, respectively. More preferably, they are present in a range 70 to 30% to 30 to 70% w/w, respectively.

15 The mixed amorphous silica fibres within the substrate are preferably randomly orientated in the x and y direction (in-plane), producing a two-dimensional isotropic structure. Additionally, random orientation in the z direction (through-plane) can be introduced with the inclusion of very short fibres, typically lengths of less than or equal to 0.2mm or very fine  
20 fibres, typically of diameters less than or equal to 1 $\mu$ m. The fibres typically have a diameter in the range of from 0.1 $\mu$ m to 50 $\mu$ m, preferably 0.2 $\mu$ m to 20 $\mu$ m and, more preferably, about 0.4 $\mu$ m to 9 $\mu$ m. The fibres typically have lengths in the range of from 0.05mm to 300mm, suitably 0.5mm to 150mm, preferably 1mm to 50mm and, more preferably, about 6mm to 20mm.

25 The porous substrate typically has at least 50%, suitably at least 75%, of the individual pore sizes being greater than 1 $\mu$ m in at least one direction, although a porous substrate wherein some of the pores are less than 1 $\mu$ m in all directions is within the scope of the invention.

30 It is also necessary to coat the fibres with one or more different materials after forming the porous substrate network to act as a binder and provide the necessary physical integrity of the structure. Fibres may be coated with a solution or dispersion of ion-exchange polymeric



materials, such as Nafion® 1100EW solution, or other non-ion-conducting polymers such as PTFE, FEP, PVDF, Viton®, polyethylene and polypropylene, such as are further described below, or inorganic materials such as amorphous silica, titania, zirconia, zirconium silicate, zirconium phosphates or the like, or mixtures thereof. Solutions of ion-exchange polymers may be either organic or aqueous, and the polymer may be either in protonic form or in ion-exchanged form, wherein the proton site is replaced with, *e.g.*, Na<sup>+</sup> or t-butylammonium ion.

The substrate of the present invention is suitably for use in the preparation of a composite membrane for use in a fuel cell. When for use in a fuel cell, the total thickness of the membrane is suitably less than 200µm and preferably less than 100µm.

For its use in the preparation of a composite membrane, the substrate is preferably associated with an ion-conducting polymer. Accordingly, the present invention further provides a composite membrane comprising a porous substrate of fibres and at least one ion-conducting polymer, characterised in that the substrate comprises mixed amorphous silica fibres, as defined hereinabove, that are bound with a binder.

The substrates according to the present invention, when used as a membrane by the incorporation of an ion-conducting polymer therein, produce a surprising effect on the dimensional stability of the membrane when subject to full hydration conditions. Accordingly, when tested by the method described hereinafter in the Examples, the dimensional changes in membranes based on the substrates according to the present invention result in less than or equal to about ±9% change in their areas.

For PEM fuel cell applications, the ion-conducting polymer is a proton-conducting polymer, examples of such polymers being well known to those skilled in the art. More than one proton-conducting polymer may be present and/or a non-ion-conducting polymer may also be included in the novel membrane of the invention.

The proton conducting polymers suitable for use in the present invention may include, but are not limited to:

1) Polymers which have structures with a substantially fluorinated carbon chain optionally having attached to it side chains that are substantially fluorinated. These polymers contain sulphonic acid groups or derivatives of sulphonic acid groups, carboxylic acid groups or derivatives of carboxylic acid groups, phosphonic acid groups or derivatives of phosphonic acid groups, phosphoric acid groups or derivatives of phosphoric acid groups and/or mixtures of these groups. Perfluorinated polymers include Nafion<sup>®</sup>, Flemion<sup>®</sup> and Aciplex<sup>®</sup> commercially available from E. I. DuPont de Nemours (U.S. Patents 3,282,875; 4,329,435; 4,330,654; 4,358,545; 4,417,969; 4,610,762; 4,433,082 and 5,094,995), Asahi Glass KK and Asahi Chemical Industry respectively. Other polymers include those covered in U.S. Patent 5,595,676 (Imperial Chemical Industries plc) and U.S. Patent 4,940,525 (Dow Chemical Co.)

2) Perfluorinated or partially fluorinated polymers containing aromatic rings such as those described in WO 95/08581, WO 95/08581 and WO 97/25369 (Ballard Power Systems) which have been functionalised with SO<sub>3</sub>H, PO<sub>2</sub>H<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>, COOH, OSO<sub>3</sub>H, OPO<sub>2</sub>H<sub>2</sub>, OPO<sub>3</sub>H<sub>2</sub>. Also included are radiation or chemically grafted perfluorinated polymers, in which a perfluorinated carbon chain, for example, PTFE, fluorinated ethylene-propylene (FEP), tetrafluoroethylene-ethylene (ETFE) copolymers, tetrafluoroethylene-perfluoroalkoxy (PFA) copolymers, poly (vinyl fluoride) (PVF) and poly (vinylidene fluoride) (PVDF) is activated by radiation or chemical initiation in the presence of a monomer, such as styrene, which can be functionalised to contain an ion exchange group.

3) Fluorinated polymers such as those disclosed in EP 0 331 321 and EP 0345 964 (Imperial Chemical Industries plc) containing a polymeric chain with pendant saturated cyclic groups and at least one ion exchange group which is linked to the polymeric chain through the cyclic group.

4) Aromatic polymers such as those disclosed in EP 0 574 791 and US Patent 5,438,082 (Hoechst AG) for example sulphonated polyaryletherketone. Also aromatic polymers such as polyether sulphones which can be chemically grafted with a polymer with ion exchange functionality such as those disclosed in WO 94/16002 (Allied Signal Inc.).

5) Nonfluorinated polymers include those disclosed in U.S. Patent 5,468,574 (Dais Corporation) for example hydrocarbons such as styrene-(ethylene-butylene)-styrene, styrene-(ethylene-propylene)-styrene and acrylonitrile-butadiene-styrene co- and terpolymers where the styrene components are functionalised with sulphonate, phosphoric and/or phosphonic groups.

6) Nitrogen containing polymers including those disclosed in U.S. Patent 5,599,639 (Hoechst Celanese Corporation), for example, polybenzimidazole alkyl sulphonic acid and polybenzimidazole alkyl or aryl phosphonate.

7) Any of the above polymers which have the ion exchange group replaced with a sulphonyl chloride ( $\text{SO}_2\text{Cl}$ ) or sulphonyl fluoride ( $\text{SO}_2\text{F}$ ) group rendering the polymers melt processable. The sulphonyl fluoride polymers may form part of the precursors to the ion exchange membrane or may be arrived at by subsequent modification of the ion exchange membrane. The sulphonyl halide moieties can be converted to a sulphonic acid using conventional techniques such as, for example, hydrolysis.

10

Non-ion conducting polymeric materials which may be used in addition to the one or more ion conducting or proton conducting polymers include PTFE, FEP, PVDF, Viton® and hydrocarbon types such as polyethylene, polypropylene and polymethylmethacralate.

15

Other ion-conducting polymeric materials which are not proton conducting polymers may be used in the filler material. For example, such polymers can be used for applications requiring a bipolar membrane or a completely anion exchange membrane. Anion exchange polymers are generally based on quaternary ammonium groups, rather than the fixed sulphonic acid groups in proton conducting polymers. These include, for example, the tetraalkyl ammonium group ( $-\text{N}^+\text{R}_3$ ) and the quaternary ammonium centre in Tosflex® membranes ( $-\text{N}(\text{R}_1)(\text{CH}_2)_7\text{N}^+(\text{R}_3)$ ) supplied by Tosoh. However, it can be envisaged that all of the proton exchange polymers described above could have anion exchange equivalents.

20

The polymer is suitably applied to the coated fibres (substrate) in the form of a solution, the solvents of which may be either organic or aqueous based. Solvents of all of the above polymers may include or may be modified to include, water, methanol and/or other aliphatic alcohols, ethers, acetone, tetrahydrofuran (THF), n-methyl-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMAc), or protonic solvents such as sulphuric acid or phosphoric acid, and/or mixtures of the above. However, it has been found that an essentially aqueous solution of the polymer as described in EP 0 731 520 is preferred.

25

30

A flexible free-standing, dimensionally stable composite membrane is produced by using the substrate of the present invention, resulting in greater handlability. The membrane of the invention is therefore also more amenable to high volume, continuous production processes, as described hereinafter. The high dimensional stability of the membrane enables  
5 thinner membranes to be produced, which are more amenable to higher volume MEA manufacturing processes than are current membranes, at similar thicknesses. Current materials show very large dimensional changes with changes in the levels of water content that occur during MEA fabrication, and are therefore very difficult to handle during the MEA fabrication process.

10 In a further embodiment, a laminated membrane comprising more than one polymer-containing layer is provided, at least one layer of which is a composite membrane of the invention. Where a laminated membrane is formed that comprises more than one composite membrane layer of the invention, each layer may comprise either the same or different types  
15 of fibres and porous substrates, and also the same or different types of polymeric material embedded within the porous substrate of each composite membrane layer. Using such a laminated structure, it is possible, for example, to tailor the properties of the laminate membrane opposed to the anode and cathode sides in the MEA of a proton exchange membrane fuel cell, for example, to improve water management in the fuel cell, or to be able  
20 to use lower cost proton-conducting polymers to form a substantial part of the laminate membrane.

Composite membranes comprising the substrate of the present invention are suitable for low cost manufacture, and the substrates and membranes may be manufactured by:

- 25 (i) forming a porous substrate of, preferably randomly orientated individual, mixed amorphous silica fibres by adapting a continuous manufacturing process, which for example may be based on wet lay processes such as those employed in paper-making, or dry lay processes employed, for example, to produce non-woven fabrics and felts; and, optionally, thereafter,
- 30 (ii) impregnating the fibre matrix substrate with the polymeric material to produce a membrane. This can be done by any number of coating processes such as printing, rolling, K-bar, doctor blade methods, spraying or thin-film casting.

For example, in a process based on a paper-making technology to prepare a composite membrane, the fibres are dispersed in water to form a dilute slurry and thereafter a continuous structure is formed by the controlled deposition of said slurry onto a moving mesh bed, de-watering the solids, and drying and compacting the fibre network. The solution containing the dispersion of the binder material can be applied either at the wet end of the process, *i.e.* before the drying stage, or after the network has been dried. This is followed by nip roller coating of the substrate to fill it with a solution of the ion-conducting polymeric material, and further compaction and drying of the membrane under a suitable time, temperature and pressure regime to produce the final thin film or sheet of fibre/polymer composite membrane.

A major advantage of using a continuous manufacturing method, such as a conventional paper making technique, is that the composite membrane is easily manufactured in a fewer number of steps than prior art composite membranes, thus making it more cost-effective and commercially viable. The membrane may also be produced in continuous lengths of many metres and widths of equal to or greater than one metre. A further advantage is that it is possible to combine a membrane of the present invention with one or more electrode layers as described in European patent specification number EP 0 791 974 to form a membrane electrode assembly at the same rate as each individual component could be produced.

The present invention also relates to a membrane electrode assembly and a method for the manufacture thereof, wherein the composite membrane is one according to the present invention. A still further aspect of the present invention relates to a fuel cell and a method for the manufacture thereof, which fuel cell comprises a composite membrane of the present invention.

The present invention is not limited to the use of the composite membrane in a fuel cell and any electrochemical device which comprises a composite membrane of the invention is within the scope.

The present invention will now be described by way of example only which is not intended to be limiting thereof.

### EXAMPLE 1

#### PREPARATION OF MIXED AMORPHOUS SILICA/ALCOHOLIC NAFION@ SUBSTRATE

5

A mixture of chopped silica fibres (Type QC9/33-20mm from Quartz et Silice BP 521-77794 Nemours, Cedex, France) (0.18g), and silica microfibre (Q fibre, type 106 from Johns Manville, Insulation Group, PO Box 5108, Denver, CO, USA) (0.37g) were dispersed with mixing, in water (3000ml). A non-woven matrix was fabricated from the  
10 resulting mixture in a single-step process, based on the principles of paper-making technology, as a sheet size of 855cm<sup>2</sup> (33cm diameter) in a sheet former (design based on standard SCA Sheet former from AB Lorentzen & Wettre, Box 4, S-163 93 Stockholm, Sweden). The fibre sheet was removed from the wire and air dried at 150°C.

15

The non-woven sheet was sprayed with a 5% solution of Nafion®, 1100 EW in lower aliphatic alcohols (Solutions Technologies Inc, Mendenhall, PA 19357, USA) to give a dry Nafion® loading of 0.78g.

### EXAMPLE 2

20

#### PREPARATION OF MIXED AMORPHOUS SILICA/PTFE/SILICA SUBSTRATE

A non-woven matrix was fabricated according to the method and materials of Example 1. The fibre sheet, as formed on the wire and whilst still wet, was sprayed with a  
25 binder solution comprising a 10wt% aqueous dispersion of polytetrafluoroethylene (Teflon GP1®; ICI Chemicals and Polymers Ltd, PO Box 4, Thornton, Cleveleys, Blackpool, FY5 4QD) and a 10wt% solution of colloidal silica (Syton® T40AS; DuPont Speciality Chemicals, Havennummer 500, Wilmington Straat, 2030 Antwerp, Belgium) in a 1:1 ratio to give a loading of 0.27g of the Teflon/silica mixture. The sheet was removed from the wire and air  
30 dried at 150°C, then fired in air at 280°C

### EXAMPLE 3

#### PREPARATION OF MIXED AMORPHOUS SILICA/SILICA SUBSTRATE

5 A non-woven matrix was fabricated according to the method and materials of Example 1. The fibre sheet, as formed on the wire and whilst still wet, was sprayed with a binder solution comprising a 20wt% solution of colloidal silica (Syton® T40AS; DuPont Speciality Chemicals, Havennummer 500, Wilmington Straat, 2030 Antwerp, Belgium) to give a loading of 0.1g of the silica. The sheet was removed from the wire and air dried at  
10 150°C.

### COMPARATIVE EXAMPLES

#### NAFION® 1135, 115 & 117 MEMBRANES

15 Nafion® membrane type 1135 (produced by E I DuPont de Nemours, Polymer Products Department, Fayetteville, NC, USA) was used as received. A 10x10cm square was cut from the bulk membrane. A measurement of the membrane's mass was taken before the sample was placed in a sealable polyethylene bag of known weight. With the bag seal open,  
20 the membrane was dried overnight (~16 h) at 40°C under vacuum (~10mbar). After releasing the vacuum, the bag was quickly sealed before being weighed. [Mass loss from the membrane and bag together was adjusted for the average mass loss from three identical bags containing no membrane]. Lengths in the x and y directions were measured whilst the dried membrane was still in the sealed bag to establish the dehydrated dimensions.

25 The membrane was placed in 2 litres of de-ionised water, heated to boiling and maintained at boiling for 90 minutes. The membrane was then removed from the de-ionised water and the excess surface water removed by blotting with filter paper. The x and y dimensions were then measured using the same procedure as before.

30

Nafion® membranes types 115 and 117 (also produced by E I DuPont de Nemours, Polymer Products Department, Fayetteville, NC, USA) were also used as received. A 10x10cm square was cut from each bulk membrane and treated according to the above procedure.

5

The dimensional changes and area change for each comparative membrane are recorded in Table 1.

#### EXAMPLE 4

10

#### PREPARATION OF TRIPLE LAMINATE MEMBRANES USING SUBSTRATE OF EXAMPLE 1

The non-woven silica fibre/binder matrix prepared according to Example 1 was placed on a sheet of sintered PTFE and a solution of perfluorosulphonic acid (Nafion® produced by E I DuPont de Nemours) in the aqueous form as described in EP 731 520 was applied to the silica fibre matrix. The structure was filled with the aqueous Nafion® to achieve a total solid Nafion® loading of 6.55mg/cm<sup>2</sup>.

A further two sheets were prepared in the same fashion. The three sheets were placed on top of each other and sandwiched between two thin, non-porous PTFE sheets. The sandwich was pressed at 90 to 100psig for six minutes at 177°C to produce a triple laminate membrane.

A 10x10cm square was cut from the bulk membrane and treated by the same procedure as described in the Comparative Examples. The results are recorded in Table 1.



**EXAMPLE 5****PREPARATION OF TRIPLE LAMINATE MEMBRANES USING SUBSTRATE  
OF EXAMPLE 2**

5

The non-woven silica fibre/binder matrix prepared according to Example 2 was treated according to the method and materials of Example 4 (total solid Nafion® loading of 7.3mg/cm<sup>2</sup>) to produce a triple laminate membrane, whose results also appear in Table 1.

10

**EXAMPLE 6****PREPARATION OF TRIPLE LAMINATE MEMBRANES USING SUBSTRATE  
OF EXAMPLE 3**

15

The non-woven silica fibre/binder matrix prepared according to Example 3 was treated according to the method and materials of Example 4 (total solid Nafion® loading of 7.29mg/cm<sup>2</sup>) to produce a triple laminate membrane, whose results also appear in Table 1.

**EXAMPLE 7**

20

**PREPARATION OF SINGLE SHEET MEMBRANES USING SUBSTRATE OF  
EXAMPLE 1**

25 A single sheet of the non-woven mixed silica fibre matrix with the sprayed alcoholic Nafion® binder was formed as described in Example 1 and filled with a solution of perfluorosulphonic acid (Nafion® produced by E I DuPont de Nemours) in the aqueous form as described in EP 731 520 to achieve a total solid Nafion® loading of 6.49mg/cm<sup>2</sup>.

30 The sheet was sandwiched between two thin, non-porous PTFE sheets. The sandwich was pressed at 90 to 100psig for six minutes at 177°C to produce a membrane.

A 10x10cm square was cut from the bulk membrane and treated by the same procedure as described in the Comparative Examples. The results are recorded in Table 1.

#### **EXAMPLE 8**

5

#### **PREPARATION OF SINGLE SHEET MEMBRANES USING SUBSTRATE OF EXAMPLE 2**

The non-woven silica fibre/binder matrix prepared according to Example 2 was treated according to the method and materials of Example 7 (total solid Nafion® loading of 7.24mg/cm<sup>2</sup>) to produce a membrane whose results also appear in Table 1.

#### **EXAMPLE 9**

15

#### **PREPARATION OF SINGLE SHEET MEMBRANES USING SUBSTRATE OF EXAMPLE 3**

The non-woven silica fibre/binder matrix prepared according to Example 2 was treated according to the method and materials of Example 7 (total solid Nafion® loading of 6.38mg/cm<sup>2</sup>) to produce a membrane whose results also appear in Table 1.

20

**TABLE 1****SILICA MIXED FIBRE MEMBRANES**

Example Number	Membrane	Binder Type	Post-boil Dimensional Changes		
			x (%)	y (%)	Area (%)
CP	Nafion® 1135	N/A	+4.1	+25.0	+30.0
CP	Nafion® 115	N/A	+15.8	+20.5	+39.0
CP	Nafion® 117	N/A	+13.4	+22.5	+39.0
4	triple laminate	alcoholic Nafion®	+0.5	0	+0.5
5	triple laminate	1:1 colloidal silica/PTFE	+1.5	+3.0	+4.6
6	triple laminate	colloidal silica	+3.0	+2.0	+5.6
7	single sheet	alcoholic Nafion®	-1.0	-1.0	-2.0
8	single sheet	1:1 colloidal silica/PTFE	-4.0	-4.5	-8.0
9	single sheet	colloidal silica	-1.0	-2.0	-3.0

**CLAIMS**

1. A substrate, suitable for the preparation of a composite membrane, which substrate comprises a porous matrix of fibres, characterised in that the fibres comprise mixed  
5 amorphous silica fibres that are bound with a binder.
2. A substrate according to claim 1, wherein the mixed amorphous silica fibres comprise micro-fine amorphous silica fibres.
- 10 3. A substrate according to claim 1 or claim 2, wherein the mixed amorphous silica fibres comprise one or more chopped strand(s) of amorphous silica.
4. A substrate according to any preceding claim wherein the amorphous silica fibres comprise a mixture of both microfibrils and chopped fibres in the range of from 95:5%  
15 to 5:95% by weight of the mixture respectively.
5. A substrate according to claim 4 wherein the amorphous silica fibres comprise a mixture of both microfibrils and chopped fibres in the range of from 70:30% to 30:70%  
by weight of the mixture respectively.  
20
6. A substrate according to any preceding claim wherein the fibres have a diameter in the range of from 0.1 $\mu$ m to 50 $\mu$ m.
7. A substrate according to claim 6 wherein the fibres have a diameter in the range of  
25 from 0.4 $\mu$ m to 9 $\mu$ m.
8. A substrate according to any preceding claim, wherein the binder comprises a solution or dispersion of ion-exchange polymeric materials, or non-ion-conducting polymers, or inorganic materials or mixtures thereof.

9. A substrate according to any preceding claim for use in the preparation of a composite membrane.
10. A composite membrane comprising a porous substrate of fibres and at least one ion-conducting polymer, characterised in that the substrate is one according to any preceding claim, which comprises mixed amorphous silica fibres bound with a binder.
11. A composite membrane according to claim 10, which when tested by the method described herein in the Examples, results in less than or equal to about  $\pm 9\%$  change in the area.
12. A composite membrane according to claim 10 or claim 11 wherein the total thickness of the membrane is less than  $200\mu\text{m}$ .
13. A composite membrane according to any one of claims 10 to 12 for use in a fuel cell.
14. A process for the manufacture of a substrate according to any one of claims 1 to 9, which process comprises
  - (a) dispersing the fibres in water to form a slurry;
  - (b) depositing the slurry onto a mesh bed to form a network;
  - (c) drying and compacting the fibre network; and
  - (d) applying, before or after step (c), a dispersion of binder.
15. A process for the manufacture of a membrane according to any one of claims 10 to 13, which process comprises
  - (i) forming a porous substrate of, preferably randomly orientated individual mixed amorphous silica fibres bound with a binder by a process according to claim 14; and, thereafter,
  - (ii) impregnating the porous substrate with a polymeric material to produce a membrane.

16. A process according to claim 15, wherein step (ii) is carried out by nip roller coating of the substrate to fill it with a solution of ion-conducting polymeric material, and further compaction and drying of the membrane.
- 5 17. A membrane electrode assembly comprising a substrate according to any one of claim 1 to 9 and/or a composite membrane according to any one of claims 10 to 13.
18. A fuel cell comprising a substrate according to any one of claim 1 to 9 and/or a composite membrane according to any one of claims 10 to 13.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02935

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08J5/22 H01M8/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J H01M B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP 0 875 524 A (JOHNSON MATTHEY PLC) 4 November 1998 (1998-11-04)  claims 1,2,5,7,9,14-16,21,23	1,6, 8-10,12, 13
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-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02935

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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